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(54) Title: WAX HYDROISOMERIZATION PROCESS

(57) Abstract

This invention discloses a process for producing a high Viscosity Index lubricant having a viscosity of at least 125 from a waxy hydrocarbon feed having a wax content of at least 40 wt.%. The process comprises catalytically dewaxing waxy paraffins present in the feed primarily by isomerization, in the presence of hydrogen and in the presence of a low acidity large pore zeolite molecular sieve having a crystal size of less than 0.1 micron, an alpha value of not more than 30 and containing a noble metal hydrogenation component. The large pore zeolite is preferably zeolite beta loaded with 0.3 to 2 wt.% Pt. The feed may be hydrocracked prior to dewaxing with the large pore zeolite. The effluent of the process may also be further dewaxed by either solvent or catalytic means in order to achieve target pour point.

# WAX HYDROISOMERIZATION PROCESS

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related to co-pending application
Serial No. 08/017,949 (continuation of S.N. 07/548,702)
entitled Production of High Viscosity Index Lubricants,
which describes a two-step process for producing high
Viscosity Index lubricants by hydrocracking and
hydroisomerization of petroleum wax feeds using a low
acidity zeolite beta hydroisomerization catalyst.  Serial
No. 08/017,955, also entitled Production of High Viscosity
Index Lubricants, describes a wax hydroisomerization
process using zeolite catalysts of controlled low acidity
at high pressures. The instant application is a
continuation-in-part of Serial No. 08/017,955.  The instant
application is also a continuation-in-part of Serial No.
08/017,949.  Serial No. 08/017,955 is incorporated by
reference in the instant application.  Corresponding
European Patent No. 464,547A1, (which specifies the use of
low acidity zeolite beta for wax isomerization) is also
incorporated by reference.  The instant application is
also related to co-pending application S.N. 08/303,091, in
which two dewaxing catalysts operate synergistically to
produce a lubricant of high Viscosity Index.

## FIELD OF THE INVENTION

This invention relates to the production of high
Viscosity Index lubricants by isomerizing petroleum waxes
using large pore zeolites of small crystal size.  The waxes
may be hydrocracked prior to isomerization.  The
isomerization product may be further dewaxed by either
solvent or catalytic means in order to achieve a target
pour point.

BACKGROUND OF THE INVENTION

Mineral oil based lubricants are conventionally produced by a separative sequence carried out in the petroleum refinery which comprises fractionation of a paraffinic crude oil under atmospheric pressure followed by fractionation under vacuum to produce distillate fractions (neutral oils) and a residual fraction which, after deasphalting and severe solvent treatment may also be used as a lubricant basestock. This refined residual fraction is usually referred to as bright stock. Neutral oils, after solvent extraction to remove low viscosity index (V.I.) components, are conventionally subjected to dewaxing, either by solvent or catalytic dewaxing processes, to achieve the desired pour point. The dewaxed lube stock may be hydrofinished to improve stability and remove color bodies. Viscosity Index (V.I.) is a reflection of the amount of viscosity decrease a lubricant undergoes with an increase in temperature. The products of solvent dewaxing are dewaxed lube oil and slack wax. Slack wax typically contains 60% to 90% wax with the balance being entrained oil. In some instances it is desirable to purify the slack wax of entrained oil by subjecting the slack wax to a deoiling step in which the slack wax is diluted with dewaxing solvents and filtered at a temperature higher than that used in the filtering step used to produce the slack wax. The purified wax is termed deoiled wax, and contains greater than 95% wax. The byproduct of the second filtration typically contains 50% wax and is termed foots oil.

Catalytic dewaxing of lube stocks is accomplished by converting waxy molecules to light products by cracking, or by isomerizing waxy molecules to form species which remain in the dewaxed lube. Dewaxing catalysts preserve high yield primarily by having pore structures which inhibit cracking of cyclic and highly branched species, those generally associated with dewaxed lube, while permitting easier access to catalytically active sites to near-linear

molecules, of which wax is generally composed. Catalysts
which significantly reduce the accessibility of species on
the basis of molecular size are termed shape selective.
Increasing the shape selectivity of a dewaxing catalyst
will frequently increase the yield of dewaxed oil.

The shape selectivity of a dewaxing catalyst is
limited practically by its ability to convert waxy
molecules which have a slightly branched structure. These
types of species are more commonly associated with heavier
lube stocks, such as bright stocks. Highly shape selective
dewaxing catalysts may be unable to convert heavy, branched
wax species leading to a hazy lube appearance at ambient
temperature and high cloud point relative to pour point.

Conventional lube refining techniques rely upon the
proper selection and use of crude stocks, usually of a
paraffinic character, which produce lube fractions with
desired qualities in adequate amounts. The range of
permissible crude sources may, however, be extended by the
lube hydrocracking process which is capable of utilizing
crude stocks of marginal or poor quality, usually with a
higher aromatic content than the best paraffinic crudes.
The lube hydrocracking process, which is well established
in the petroleum refining industry, generally comprises an
initial hydrocracking step carried out under high pressure,
at high temperature, and in the presence of a bifunctional
catalyst which effects partial saturation and ring opening
of the aromatic components which are present in the feed.
The hydrocracked product is then subjected to dewaxing in
order to reach the target pour point since the hydrocracked
product usually contains species with relatively high pour
points. Frequently the liquid product from the dewaxing
step is subjected to a low temperature, high pressure
hydrotreating step to reduce the aromatic content of the
lube to the desired level.

Current trends in the design of automotive engines are
associated with higher operating temperatures as the
efficiency of the engines increases. These higher

operating temperatures require successively higher quality
lubricants.  One of the requirements is for higher
viscosity indices (V.I.) in order to reduce the effects of
the higher operating temperatures on the viscosity of the
engine lubricants.  High V.I. values have conventionally
been attained by the use of V.I. improvers e.g.
polyacrylates and polystyrenes.  V.I. improvers tend to
undergo degradation due to high temperatures and high shear
rates encountered in the engine.  The more stressing
conditions encountered in high efficiency engines result in
even faster degradation of oils which employ significant
amounts of V.I. improvers.  Thus, there is a continuing
need for automotive lubricants which are based on fluids of
high Viscosity Index and which are resistant to the high
temperature, high shear rate conditions encountered in
modern engines.

Synthetic lubricants produced by the polymerization of
olefins in the presence of certain catalysts have been
shown to possess excellent V.I. values, but they are
relatively expensive to produce.  There is therefore a need
for the production of high V.I. lubricants from mineral oil
stocks which may be produced by techniques comparable to
those presently employed in petroleum refineries.

U.S. Patent No. 4,975,177 discloses a two-stage
dewaxing process for producing lube stocks of high V.I.
from waxy feedstocks.  In the first stage of this process,
the waxy feed is catalytically dewaxed by isomerization
over zeolite beta containing a noble metal.  The examples
employ pressures below 6996 kPa$_a$ (1000 psig) and a catalyst
of moderate acidity, with an alpha value of about 55.  The
product of the isomerization step still contains waxy
species and requires further dewaxing to meet target pour
point.  The second-stage dewaxing employs either solvent
dewaxing, in which case the rejected wax may be recycled to
the isomerization stage to maximize yield, or catalytic
dewaxing.  Catalysts which may be used in the second stage
are ZSM-5, ZSM-22, ZSM-23, and ZSM-35.  To preserve yield

and V.I., the second stage dewaxing catalyst should have
selectivity similar to solvent dewaxing. U.S. Patent
4,919,788 also teaches a two-stage dewaxing process in
which a waxy feed is partially dewaxed by isomerization
over a siliceous Y or beta catalyst containing a noble
metal. Examples indicate pressures below 10030 kPa, and a
zeolite beta catalyst of moderate acidity with an alpha
value of 55. This product is subsequently dewaxed to
desired pour point using either solvent dewaxing or
catalytic dewaxing. Dewaxing catalysts with high shape
selectivity, such as ZSM-22 and ZSM-23, are preferred
catalysts.

Serial No. 08/017,949 discloses a two stage
hydrocracking and hydroisomerization process. The first
stage employs a bifunctional catalyst comprising a metal
hydrogenation component on an amorphous acidic support.
The second stage, the hydroisomerization step, is carried
out over zeolite beta. Subsequent dewaxing is optional but
recommended. Either solvent dewaxing or catalytic dewaxing
maybe used subsequently in order to obtain target V.I. and
pour point.

In S.N. 08/017,955, petroleum wax feed is subjected to
hydroisomerization over a noble metal-containing zeolite
catalyst of low acidity. The paraffins present in the feed
are selectively converted to iso-paraffins of high V.I. but
lower pour point so that a final lube product of good
viscometric properties is produced with a minimal degree of
subsequent dewaxing. The process, which operates under
high pressure, is well suited for upgrading waxy feeds such
as slack wax with aromatic contents greater than about 15
wt% to high Viscosity Index lubricating oils with high
single pass yields and limited requirement for product
dewaxing.

U.S. Pat. No. 5,302,279 (and the analogous European
patent application EP 464 547 A1) teaches the use of a low
acidity form of zeolite beta for isomerizing and dewaxing
furfural raffinates. The improved selectivity of a

catalyst of low acidity over one of high acidity was
demonstrated in the examples.

    U.S. Pat. No. 5,282,958 has demonstrated improved
isomerization selectivity for n-hexadecane using unipore
zeolites of small crystal size, although the crystal sizes
quoted are all extremely small and are inconsistent with
measurements made by others in the field of catalyst
preparation. Additionally, constrained intermediate pore
zeolites such as ZSM-22 and ZSM-23, which are used in this
patent, do not permit access to the framework of the
catalyst as readily as other intermediate and large pore
molecular sieves. Reactions of lubricant-type molecules
are likely to occur near the pore mouth of intermediate
pore catalysts. The crystal size of ZSM-22 or ZSM-23 is
not likely to impact isomerization selectivity as strongly
as for catalysts with a less restrictive pore structure.

SUMMARY OF THE INVENTION

    The concept of the instant invention involves a
process for isomerizing and dewaxing waxy feedstocks using
large pore molecular sieves with small crystal size for
producing high quality, high VI lubricant base stocks.
Large pore molecular sieves applicable to this invention
are defined as having a Constraint Index less than one and
include zeolites beta, mordenite and Y. Large pore
molecular sieves have accessible pore structures for
forming highly branched paraffins from waxy feed stocks,
particularly those stocks containing high molecular weight
species. Such branched paraffins have a high VI and low
pour point. Because isomerization occurs within the pores
of the catalyst, small crystal size enables branched
paraffins to readily diffuse from the zeolite pores without
cracking, thus resulting in high lube yields.

    The instant invention involves processing a waxy
hydrocarbon feedstock over an isomerization catalyst which
converts waxy species to branched paraffins. The formation
of these branched paraffins which have high viscosity

Indices and low pour points, results in a lubricant base
stock having superior quality.

The feedstocks used in this invention contain at least
20% wax and preferably contain more than 30% wax. More
preferably they contain more than 50% wax. The feedstock
may be pretreated prior to isomerization to remove nitrogen
and sulfur-containing species and to reduce its aromatics
content. The raw or pretreated feedstock is contacted with
a noble metal-containing low-acidity large pore molecular
sieve over which a substantial fraction of the wax in the
feed is isomerized to form species typically associated
with lube base stocks. A large pore catalyst is defined as
one which has at least one channel comprising 12-membered
oxygen rings. Isomerization occurs typically at a pressure
between 4238 $kPa_a$ (600 psig) and 20,786 $kPa_a$ (3000 psig).
The effluent from isomerization may be hydrotreated to
remove residual aromatics. The zeolite beta catalyst
discussed in the examples of this invention has a crystal
diameter of less than 0.1 microns in order to maximize the
relative rates of isomerization to cracking. Small
diameter crystals allow isomerized species to diffuse
readily from the catalyst framework, thereby reducing the
potential for their cracking. The prior art, discussed in
the Background, supra, demonstrates improved selectivity of
a catalyst of low acidity over one of higher acidity. Low
zeolitic acidity coupled with high metals activity is
necessary for high isomerization selectivity but does not
guarantee such selectivity. The crystal size of the
certain molecular sieves has been found to be an important
factor impacting isomerization selectivity. Large crystals
increase the diffusion path for isomerized species to exit
the framework, thus increasing the possibility that the
isomerized molecule will crack within the framework. The
invention detailed here illustrates the selectivity benefit
for isomerizing waxy feeds, such as slack waxes, with a
small crystal, low-acidity zeolite beta catalyst.

The instant invention employs zeolite beta loaded with
a noble metal such as Pt to selectively isomerize waxy
species to high VI lubricants.  This catalyst has high
isomerization selectivity, tolerance for moderate levels of
sulfur and nitrogen, and an accessible pore structure to
permit conversion of bulky wax molecules.  The selectivity
of zeolite beta loaded with Pt is optimized if it has low
zeolitic acidity, high metals dispersion and small crystal
size.

## DESCRIPTION OF THE DRAWING

The Figure compares the selectivity for wax
isomerization for two low-acidity silica-bound zeolite beta
catalysts loaded with Pt.  One possesses a small crystal
size and the other possesses a large crystal size.

## DETAILED DESCRIPTION OF THE INVENTION

In the present process feeds with a relatively high
wax content are converted to high V.I. lubricants in a
hydroisomerization process using a low acidity zeolite
hydroisomerization catalyst having a small crystal size.
Subsequent dewaxing may be required to remove residual wax
from the isomerization step.  The products are
characterized by good viscometric properties including high
viscosity index, typically at least 140 at -17.78°C (0°F)
pour point and usually in the range 143 to 147.

### Feed

The processes of the instant invention are capable of
operating with a wide range of feeds of mineral oil origin
to produce a range of lubricant products with good
performance characteristics.  Such characteristics include
low pour point, low cloud point, and high Viscosity Index.
The quality of the product and the yield in which it is
obtained is dependent upon the quality of the feed and its
amenability to processing by the catalysts of the instant
invention.  Products of the highest V.I. are obtained by

using preferred wax feeds such as slack wax, foots oil,
deoiled wax or vacuum distillates derived from waxy crudes.
Waxes produced by Fischer-Tropsch processing of synthesis
gas may also be used as feedstocks. Products with lower
V.I. values may also be obtained from other feeds which
contain a lower initial quantity of waxy components.

The feeds which may be used should have an initial
boiling point which is no lower than the initial boiling
point of the desired lubricant. A typical initial boiling
point of the feed exceeds 343°C (650°F). Feeds of this
type which may be used include vacuum gas oils as well as
other high boiling fractions such as distillates from the
vacuum distillation of atmospheric resids, raffinates from
the solvent extraction of such distillate fractions,
hydrocracked vacuum distillates and waxes from the solvent
dewaxing of raffinates and hydrocrackates.

The feed may require preparation in order to be
treated satisfactorily in the hydroisomerization step. The
preparation steps which are generally necessary are those
which remove low V.I. components such as aromatics and
polycyclic naphthenes, as well as nitrogen and sulfur
containing species.

Suitable pre-treatment steps for preparing feeds for
the hydroisomerization are those which remove the aromatics
and other low V.I. components from the initial feed.
Hydrotreatment is an effective pretreatment step,
particularly at high hydrogen pressures which are effective
for aromatics saturation e.g. 5,600 kPa$_a$ (800 psig) or
higher. Mild hydrocracking may also be employed as
pretreatment and is preferred in the instant invention, if
pretreatment is required. Example 3, infra, discusses the
hydrocracking conditions employed in the instant invention
in order to prepare a feed for the dewaxing process.
Pressures over 6996 kPa$_a$ (1000 psig) are preferred for
hydrocracking treatment. Hydrocracking removes nitrogen
containing and sulfur-containing species and reduces
aromatics content as Table 6 below illustrates.

Hydrocracking, in this example, has also slightly altered the boiling range of the feed, causing it to boil in a lower range. Commercially available catalysts such as fluoride nickel-tungsten on alumina (NiWF-/$Al_2O_3$) may be

5    employed for the hydrocracking pretreatment.

The preferred gas oil and vacuum distillate feeds are those which have a high wax content, as determined by ASTM D-3235, preferably over about 30 wt% and more preferably over 50 wt%. Feeds of this type include certain South-East

10   Asian and mainland China oils. Minas Gas Oil, from Indonesia, is such a feed. These feeds usually have a high paraffin content, as determined by a conventional analysis for paraffins, naphthenes, and aromatics. The properties of typical feeds of this type are described in S.N.

15   07/017,955.

As stated previously, the wax content of the preferred feeds is high, generally at least 30 wt% (as determined by ASTM Test D-3235) prior to pretreatment. The wax content before pretreatment is more usually at least 60 to 80 wt%

20   with the balance being occluded oil comprising iso-paraffins, aromatics and naphthenics. These waxy, highly paraffinic wax stocks usually have low viscosities because of their relatively low content of aromatics and naphthenes although the high content of waxy paraffins gives them

25   melting points and pour points which render them unacceptable as lubricants without further processing. Wax feeds are discussed further in S.N. 07/017,955.

The most preferred type of wax feeds are the slack waxes, (see Table 2, infra). These are the waxy products

30   obtained directly from a solvent dewaxing process, e.g. an MEK/toluene or MEK/MIBK or propane dewaxing process. The slack wax, which is a solid to semi-solid product, comprising primarily highly waxy paraffins (mostly n- and mono-methyl paraffins) together with occluded oil, may be

35   used as such or it may be subjected to an initial deoiling step of a conventional character in order to remove the occluded oil. Removal of the oil results in a harder, more

highly paraffinic wax which may then be used as the feed.
The byproduct of the deoiling step is termed Foots Oil and
it may also be used as feed to the process.  Foots Oil
contains most of the aromatics present in the original
slack wax and with these aromatics, most of the
heteroatoms.  Slack wax and foots oil typically require
pretreatment prior to catalytic dewaxing.  The oil content
of deoiled waxes may be quite low and for this purpose,
measurement of the oil content by the technique of ASTM
D721 may be required for reproducibility, since the D-3235
test referred to above tends to be less reliable at oil
contents below about 15 wt%.

The compositions of some typical waxes are given in
Table 1 below.

### Table 1

#### Wax Composition - Arab Light Crude

|                             | A    | B    | C    | D    |
|-----------------------------|------|------|------|------|
| Paraffins, wt. pct.         | 94.2 | 81.8 | 70.5 | 51.4 |
| Mono-naphthenes, wt. pct.   | 2.6  | 11.0 | 6.3  | 16.5 |
| Poly-naphthenes, wt. pct.   | 2.2  | 3.2  | 7.9  | 9.9  |
| Aromatics, wt. pct.         | 1.0  | 4.0  | 15.3 | 22.2 |

A typical slack wax feed has the composition shown in
Table 2 below.  This slack wax is obtained from the solvent
(MEK) dewaxing of a 65 cSt at 40°C (300 SUS) neutral oil
obtained from an Arab Light crude.

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## Table 2

### Slack Wax Properties

| | |
|---|---|
| API | 39 |
| Hydrogen, wt. pct. | 15.14 |
| Sulfur, wt. pct. | 0.18 |
| Nitrogen, ppmw | 11 |
| Melting point, °C (°F) | 57 (135) |
| KV at 100°C, cSt | 5.168 |
| PNA, wt pct: | |
|     Paraffins | 70.3 |
|     Naphthenes | 13.6 |
|     Aromatics | 16.3 |

### Simulated Distillation:

| % | °C | (°F) |
|---|---|---|
| 5 | 375 | (710) |
| 10 | 413 | (775) |
| 30 | 440 | (825) |
| 50 | 460 | (860) |
| 70 | 482 | (900) |
| 90 | 500 | (932) |
| 95 | 507 | (945) |

Another slack wax suitable for use in the present process has the properties set out in Table 6 infra as part of Example 3. This wax is prepared by the solvent dewaxing of a heavy neutral furfural raffinate. As discussed previously, hydrocracking may be employed to prepare the slack wax for hydroisomerization.

## Hydrocracking Process (Optional)

If hydrocracking is employed as a pretreatment step an amorphous bifunctional catalyst is preferably used to promote the saturation and ring opening of the low quality aromatic components in the feed to produce hydrocracked products which are relatively more paraffinic. Hydrocracking is carried out under high pressure to favor aromatics saturation but the boiling range conversion is maintained at a relatively low level in order to minimize cracking of the saturated components of the feed and of the products obtained from the saturation and ring opening of

the aromatic materials. Consistent with these process
objectives, the hydrogen pressure in the hydrocracking
stage is at least about 5500 kPa. (800 psig) and usually
is in the range of 6900 kPa. (1,000 psig) to 20700 kPa.
(3,000 psig). Normally, hydrogen partial pressures of at
least 10500 kPa. (1500 psig) are best in order to obtain a
high level of aromatic saturation. Hydrogen circulation
rates of at least about 178 n.l.l.$^{-1}$ (1000 SCF/Bbl),
preferably in the range of 900 n.l.l.$^{-1}$ (2,000 SCF/Bbl) to
1800 n.l.l.$^{-1}$ (8000 SCF/Bbl) are suitable.

In the hydrocracking process, the conversion of the
feed to products boiling below the lube boiling range,
typically to 345°C- (650°F-) products is limited to no more
than 50 wt% of the feed and will usually be not more than
30 wt% of the feed in order to maintain the desired high
single pass yields which are characteristic of the process.
The actual conversion is dependent on the quality of the
feed with slack wax feeds requiring a lower conversion than
petrolatum where it is necessary to remove more low quality
polycyclic components. For slack wax feeds derived from
the dewaxing of neutral stocks, the conversion to 345°C-
(650°F-) products will, for all practical purposes not be
greater than 10 to 20 wt%, with 5-15 wt% being typical for
most slack waxes. Higher conversions may be encountered
with petrolatum feeds because they typically contain more
low quality components. With petrolatum feeds, the
hydrocracking conversion will typically be in the range of
15 to 25 wt% to produce high VI products. The conversion
may be maintained at the desired value by control of the
temperature in the hydrocracking stage which will normally
be in the range 315° to 430°C (600° to 800°F) and more
usually in the range of about 345° to 400°C (650° to
750°F). Space velocity variations may also be used to
control severity although this will be less common in
practice in view of mechanical constraints on the system.
Generally, the space velocity will be in the range of 0.25

to 2 LHSV, hr.$^{-1}$ and usually in the range of 0.5 to 1.5
LHSV.

A characteristic feature of the hydrocracking operation
is the use of a bifunctional catalyst. In general terms,
these catalysts include a metal component for promoting the
desired aromatics saturation reactions and usually a
combination of base metals is used, with one metal from the
iron group (Group VIII) in combination with a metal of
Group VIB. Thus, the base metal such as nickel or cobalt
is used in combination with molybdenum or tungsten. The
preferred combination is nickel/tungsten since it has been
found to be highly effective for promoting the desired
aromatics hydrocracking reaction. Noble metals such as
platinum or palladium may be used since they have good
hydrogenation activity in the absence of sulfur but they
will normally not be preferred. The amounts of the metals
present on the catalyst are conventional for lube
hydrocracking catalysts of this type and generally will
range from 1 to 10 wt% of the Group VIII metal and 10 to 30
wt% of the Group VI metal, based on the total weight of the
catalyst. If a noble metal component such as platinum or
palladium is used instead of a base metal such as nickel or
cobalt, relatively lower amounts are in order in view of
the higher hydrogenation activities of these noble metals,
typically from about 0.5 to 5 wt% being sufficient. The
metals may be incorporated by any suitable method including
impregnation onto the porous support after it is formed
into particles of the desired size or by addition to a gel
of the support materials prior to calcination. Addition to
the gel is a preferred technique when relatively high
amounts of the metal components are to be added e.g. above
10 wt% of the Group VIII metal and above 20 wt% of the
Group VI metal. These techniques are conventional in
character and are employed for the production of lube
hydrocracking catalysts.

The metal component of the catalyst is generally
supported on a porous, amorphous metal oxide support and

alumina is preferred for this purpose although silica-
alumina may also be employed. Other metal oxide components
may also be present in the support although their presence
is less desirable. Consistent with the requirements of a
lube hydrocracking catalyst, the support should have a pore
size and distribution which is adequate to permit the
relatively bulky components of the high boiling feeds to
enter the interior pore structure of the catalyst where the
desired hydrocracking reactions occur. To this extent, the
catalyst will normally have a minimum pore size of about 50
Å i.e with no less than about 5 percent of the pores having
a pore size less than 50 Å pore size, with the majority of
the pores having a pore size in the range of 50-400 Å (no
more than 5 percent having a pore size above 400 Å),
preferably with no more than about 30 percent having pore
sizes in the range of 200-400 Å. Preferred catalysts for
hydrocracking have at least 60 percent of the pores in the
50-200 Å range. The pore size distribution and other
properties of some typical lube hydrocracking (LHDC)
catalysts suitable for use in the hydrocracking are shown
in Table 3 below:

### Table 3

### LHDC Catalyst Properties

| | 1.5mm cyl. | 1.5 mm. tri. | 1.5 mm.cyl. |
|---|---|---|---|
| Form | | | |
| Pore Volume, cc/gm | 0.331 | 0.453 | 0.426 |
| Surface Area, m2/gm | 131 | 170 | 116 |
| Nickel, wt. pct. | 4.8 | 4.6 | 5.6 |
| Tungsten, wt. pct. | 22.3 | 23.8 | 17.25 |
| Fluorine, wt. pct. | - | - | 3.35 |
| $SiO_2/Al_2O_3$ binder | - | - | 62.3 |
| | | | |
| Real Density, gm/cc | 4.229 | 4.238 | 4.023 |
| Particle Density, gm/cc | 1.744 | 1.451 | 1.483 |
| Packing Density, gm/cc | 1.2 | 0.85 | 0.94 |

If necessary in order to obtain the desired conversion,
the catalyst may be promoted with fluorine, either by
incorporating fluorine into the catalyst during its

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preparation or by operating the hydrocracking in the presence of a fluorine compound which is added to the feed. Fluorine containing compounds may be incorporated into the catalyst by impregnation during its preparation with a
5      suitable fluorine compound such as ammonium fluoride ($NH_4F$) or ammonium bifluoride ($NH_4F \cdot HF$) of which the latter is preferred.  The amount of fluorine used in catalysts which contain this element is preferably from about 1 to 10 wt%, based on the total weight of the catalyst, usually from
10     about 2 to 6 wt%.  The fluorine may be incorporated by adding the fluorine compound to a gel of the metal oxide support during the preparation of the catalyst or by impregnation after the particles of the catalyst have been formed by drying or calcining the gel.  If the catalyst
15     contains a relatively high amount of fluorine as well as high amounts of the metals, as noted above, it is preferred to incorporate the metals and the fluorine compound into the metal oxide gel prior to drying and calcining the gel to form the finished catalyst particles.
20         The catalyst activity may also be maintained at the desired level by _in situ_ fluoriding in which a fluorine compound is added to the stream which passes over the catalyst in this stage of the operation.  The fluorine compound may be added continuously or intermittently to the
25     feed or, alternatively, an initial activation step may be carried out in which the fluorine compound is passed over the catalyst in the absence of the feed e.g. in a stream of hydrogen in order to increase the fluorine content of the catalyst prior to initiation of the actual hydrocracking.
30     _In situ_ fluoriding of the catalyst in this way is preferably carried out to induce a fluorine content of about 1 to 10 percent fluorine prior to operation, after which the fluorine can be reduced to maintenance levels sufficient to maintain the desired activity.  Suitable
35     compounds for _in situ_ fluoriding are orthofluorotoluene and difluoroethane.

The metals present on the catalyst are preferably used in their sulfide form and to this purpose pre-sulfiding of the catalyst should be carried out prior to initiation of the hydrocracking. Sulfiding is an established technique and it is typically carried out by contacting the catalyst with a sulfur-containing gas, usually in the presence of hydrogen. The mixture of hydrogen and hydrogen sulfide, carbon disulfide or a mercaptan such as butol mercaptan is conventional for this purpose. Presulfiding may also be carried out by contacting the catalyst with hydrogen and a sulfur-containing hydrocarbon oil such as a sour kerosene or gas oil.

Hydroisomerization

The paraffinic components present in the original wax feed possess high viscosity indices but have relatively high pour points. The objective of the process of the invention is, therefore, to effect a selective conversion of waxy species while minimizing conversion of more branched species characteristic of lube components. The conversion of wax occurs preferentially by isomerization to form more branched species which have lower pour points and cloud points. Some degree of cracking accompanies isomerization, the extent of cracking varying with the degree of wax conversion.

Hydroisomerization Catalyst

The catalyst used in hydroisomerization in this invention is one which has a high selectivity for the isomerization of waxy, linear or near linear paraffins to less waxy, isoparaffinic products. Catalysts of this type are bifunctional in character, comprising a metal component on a large pore size, porous support of relatively low acidity. The acidity is maintained at a low level in order to reduce conversion to products boiling outside the lube boiling range during this stage of the operation. In general terms, the catalyst should have an alpha value

below 30 prior to metals addition, with preferred values
below 20.  (See Example 1)

The alpha value is an approximate indication of the
catalytic cracking activity of the catalyst compared to a
standard catalyst.  The alpha test gives the relative rate
constant (rate of normal hexane conversion per volume of
catalyst per unit time) of the test catalyst relative to
the standard catalyst which is taken as an alpha of 1 (Rate
Constant = 0.016 sec$^{-1}$).  The alpha test is described in
U.S. Patent 3,354,078 and in J. Catalysis, 4, 527 (1965);
6, 278 (1966); and 61, 395 (1980), to which reference is
made for a description of the test.  The experimental
conditions of the test used to determine the alpha values
referred to in this specification include a constant
temperature of 538°C and a variable flow rate as described
in detail in J. Catalysis, 61, 395 (1980).

The hydroisomerization catalyst comprises a large pore
molecular sieve, generally a zeolite or
silica:aluminophosphate.  The large pore sieve is supported
by a porous binder.  Large pore zeolites usually have at
least one pore channel consisting of twelve-membered oxygen
rings.  Large pore zeolites usually have at least one pore
channel with a major dimension greater than 7A.  Zeolites
beta, Y and mordenites are examples of large pore zeolites.
The catalysts of this invention possess a crystal diameter
of less than 0.1 micron in order to maximize the relative
rates of isomerization to cracking.  Small diameter
crystals allow isomerized species to diffuse readily from
the crystal framework reducing the potential for their
cracking.

The preferred hydroisomerization catalyst employs
zeolite beta since this zeolite has been shown to possess
outstanding activity for paraffin isomerization in the
presence of aromatics, as disclosed in U.S. 4,419,220.  The
low acidity forms of zeolite beta may be obtained by
synthesis of a highly siliceous form of the zeolite e.g
with a silica-alumina ratio above about 500:1 or, more

readily, by steaming zeolites of lower silica-alumina ratio to the requisite acidity level. They may also be obtained by extraction with acids such as dicarboxylic acid, as disclosed in U.S. Patent No. 5,200,168. U.S. Patent No. 5,238,677 discloses the synthesis of dealuminated mordenite by oxalic acid extraction. U.S. Patent No. 5,164,169 discloses the preparation of highly siliceous zeolite beta employing a chelating agent such as tertiary alkenolamines in the synthesis mixture. U.S. Patent No. 3,308,069 describes the synthesis of zeolite beta with a crystal size ranging from 0.01 to 0.05 microns. Catalysts with crystal sizes of this range are used in the instant invention. The crystal size in the instant invention is not to exceed 0.1 micron, although crystal size between 0.01 and 0.05 microns are preferred.

The most preferred zeolites are severely steamed and possess a framework silica-alumina ratio above 200:1 and more preferably above 400:1.

The steaming conditions should be adjusted in order to attain the desired alpha value in the final catalyst and typically utilize atmospheres of 100 percent steam, at temperatures of from about 427° to 595°C (800° to about 1100°F). Normally, the steaming will be carried out at temperatures above 538°C (1000°F), for about 12 to 120 hours, typically about 96 hours, in order to obtain the desired reduction in acidity.

Another method of producing a low acidity zeolite beta catalyst is by replacement of a portion of the framework aluminum of the zeolite with another trivalent element such as boron which results in a lower intrinsic level of acid activity in the zeolite. The preferred zeolites of this type are those which contain framework boron. Boron is usually added to the zeolite framework prior to the addition of other metals. In zeolites of this type, the framework consists principally of silicon tetrahedral coordinated and interconnected with oxygen bridges. The minor amount of an element (alumina in the case of alumina-

silicate zeolite beta) is also coordinated and forms part
of the framework.  The zeolite also contains material in
the pores of the structure although these do not form part
of the framework constituting the characteristic structure
of the zeolite.  The term "framework" boron is used here to
distinguish between material in the framework of the
zeolite which is evidenced by contributing ion exchange
capacity to the zeolite, from material which is present in
the pores and which has no effect on the total ion exchange
capacity of the zeolite.  Zeolite beta possesses a
constraint index between 0.60 and 2.0 at temperatures
between 316°C and 399°C although Constraint Indexes less
than 1 are preferred.

Methods for preparing high silica content zeolites
containing framework boron are known and are described, for
example, in U.S. Patents Nos. 4,269,813.  A method for
preparing zeolite beta containing framework boron is
disclosed in U.S. Patent No. 4,672,049.  As noted there,
the amount of boron contained in the zeolite may be varied
by incorporating different amounts of borate ion in the
zeolite forming solution e.g. by the use of varying amounts
of boric acid relative to the forces of silica and alumina.
Reference is made to these disclosures for a description of
the methods by which these zeolites may be made.

The low acidity zeolite beta catalyst should contain at
least 0.1 wt% framework boron, preferably at least 0.5 wt%
boron.  Boron may be added to the framework prior to the
addition of other metals.  Normally, the maximum amount of
boron will be about 5 wt% of the zeolite and in most cases
not more than 2 wt% of the zeolite.  The framework will
normally include some alumina.  The silica:alumina ratio
will usually be at least 30:1, in the conditions of the
zeolite as synthesized.  A preferred boron-substituted
zeolite beta catalyst is made by steaming an initial boron-
containing zeolite containing at least 1 wt% boron (as
$B_2O_3$) to result in an ultimate alpha value no greater than
about 20 and preferably no greater than 10.

## Properties

Acidity may be reduced by the introduction of nitrogen compounds, e.g. $NH_3$ or organic nitrogen compounds, with the feed to the hydroisomerization catalyst. However, the total nitrogen content of the feed should not exceed 100 ppm and should be preferably less than 20 ppm. The catalyst may also contain metals which reduce the number of strong acid sites of the catalyst and improve the selectivity of isomerization reactions to cracking reactions. Metals which are preferred for this purpose are those belong to the class of Group IIA metals such as calcium and magnesium.

The zeolite will be composites with a matrix material to form the finished catalyst and for this purpose conventional very low-acidity matrix materials such as alumina, silica-alumina and silica are suitable although aluminas such as alpha boehmite (alpha alumina monohydrate) may also be used, provided that they do not confer any substantial degree of acidic activity on the matrixed catalyst. The zeolite is usually composited with the matrix in amounts from 80:20 to 20:80 by weight, typically from 80:20 to 50:50 zeolite:matrix. Compositing may be done by conventional means including mulling the materials together followed by extrusion into the desired finished catalyst particles. A preferred method for extruding the zeolite with silica as a binder is disclosed in U.S. 4,582,815. If the catalyst is to be steamed in order to achieve the desired low acidity, it is performed after the catalyst has been formulated with the binder, as is conventional. The preferred binder for the steamed catalyst is alumina.

The hydroisomerization catalyst also includes a metal component in order to promote the desired hydroisomerization reactions which, proceeding through unsaturated transitional species, require mediation by a hydrogenation-dehydrogenation component. In order to maximize the isomerization activity of the catalyst, metals

having a strong hydrogenation function are preferred and
for this reason, platinum and the other noble metals such
as rhenium, gold, and palladium are given a preference.
The amount of the noble metal hydrogenation component is
typically in the range 0.1 to 5 wt% of the total catalyst,
usually from 0.1 to 2 wt%.  The platinum may be
incorporated into the catalyst by conventional techniques
including ion exchange with complex platinum cations such
as platinum tetraamine or by impregnation with solutions of
soluble platinum compounds, for example, with platinum
tetraammine salts such as platinum tetraamminechloride.
The catalyst may be subjected to a final calcination under
conventional conditions in order to convert the noble metal
to its reduced form and to confer the required mechanical
strength on the catalyst.  Prior to use the catalyst may be
subjected to presulfiding as described above for the
hydrocracking pretreatment catalyst.

Hydroisomerization Conditions
        The conditions for hydroisomerization (also called
isomerization) are adjusted to achieve the objective of
isomerizing the waxy, linear and near-linear paraffinic
components in the waxy feed to less waxy but high V.I.
isoparaffinic materials of relatively lower pour point.
This end is achieved while minimizing conversion to non-
lube boiling range products 345°C- (650°F-) materials.
Since the catalyst used for hydroisomerization has a low
acidity, conversion to lower boiling products is usually at
a relatively low level and by appropriate selection of
severity, the operation of the process may be optimized for
isomerization over cracking.  At conventional space
velocities of about 1, using a Pt/zeolite beta catalyst
with an alpha value below 20, temperatures for the
hydroisomerization will typically be in the range of about
300° to 415°C (about 570° to about 780°F) with conversion
to 345°C- (650°F-) typically being from about 5 to 30 wt%,
more usually 10 to 25 wt%, of the waxy feed.

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Hydroisomerization is accomplished at hydrogen partial pressures (reactor inlet) of at least 5516 kPa$_a$ (800 psig), usually 5516 to 20785 kPa$_a$ (800 to 3000 psig) and in most cases 5516 to 17340 kPa$_a$ (800-2500 psig). Hydrogen circulation rates are usually in the range of about 90 to 900 n.l.l.$^{-1}$ (500 to 5000 SCF/Bbl). Since some saturation of aromatic components present in the original feed takes place in the presence of the noble metal hydrogenation component on the catalyst, hydrogen is consumed in the hydroisomerization even though the desired isomerization reactions are in hydrogen balance; for this reason, hydrogen circulation rates may need to be adjusted in accordance with the aromatic content of the feed and also with the temperature used in the hydroisomerization since higher temperatures will be associated with a higher level of cracking and, consequently, with a higher level of olefin production, some of which will be in the lube boiling range so that product stability will need to be assured by saturation. Hydrogen circulation rates of at least 180 n.l.l.$^{-1}$ (1000 SCF/Bbl) will normally provide sufficient hydrogen to compensate for the expected hydrogen consumption as well as to ensure a low rate of catalyst aging.

An interbed quench is desirable to maintain temperature in the process. Cold hydrogen is generally used as the quench, but a liquid quench, usually recycled product, may also be used.

Dewaxing

Although a final dewaxing step may be necessary in order to achieve the desired product pour point, depending on the wax content of the feed. It is a notable feature of the present process that the extent of dewaxing required is relatively small. Typically, the loss during the final dewaxing step will be no more than 15-20 wt% of the dewaxer feed and may be lower. Either catalytic dewaxing or solvent dewaxing may be used at this point and if a solvent

dewaxer is used, the removed wax may be recycled to the
hydroisomerization for a second pass through the
isomerization step.  The demands on the dewaxer unit for
the product are relatively low and in this respect the
present process provides a significant improvement over the
process employing solely amorphous catalysts where a
significant degree of dewaxing is required.  The high
isomerization selectivity of the zeolite catalysts enables
high single pass wax conversions to be achieved, typically
about 80% as compared to 50% for the amorphous catalyst
process so that unit throughput is significantly enhanced.

A shape-selective dewaxing catalyst maybe alternately
employed rather than a solvent dewaxing approach.  This
catalyst removes the n-paraffins together with the waxy,
slightly branched chain paraffins, while leaving the more
branched chain iso-paraffins in the process stream.  Shape-
selective catalytic dewaxing processes employ catalysts
which are more highly selective for removal of n-paraffins
and slightly branched chain paraffins than is the
isomerization catalyst, zeolite beta.  Selective catalytic
dewaxing is carried out as described in U.S. Patent No.
4,919,788, to which reference is made for a description of
this phase.  The catalytic dewaxing step in the present
process is preferably carried out with a constrained, shape
selective dewaxing catalyst based on a constrained
intermediate pore crystalline material, such as an alumino-
silicate.  A constrained intermediate crystalline material
has at least one channel of 10-membered oxygen rings with
any intersecting channel having 8-membered rings.  ZSM-23
is the preferred zeolite for this purpose although other
highly shape-selective zeolites such as ZSM-22 or the
synthetic ferrierite ZSM-35 may also be used, especially
with lighter stocks.  Silicoaluminophosphates such as SAPO-
11 and SAPO-41 maybe used as selective dewaxing catalysts.

The preferred catalysts for use as the dewaxing
catalysts are the relatively constrained intermediate pore
size zeolites.  Such preferred zeolites have a Constraint

Index in the range of 1-12, as determined by the method
described in U.S. Patent No. 4,016,218.  These preferred
zeolites are also characterized by specific sorption
properties related to their relatively constrained
diffusion characteristics.  These sorption characteristics
are those which are set out in U.S. Patent No. 4,810,357
for the zeolites such as zeolite ZSM-22, ZSM-23, ZSM-35 and
ferrierite.  These zeolites have pore openings which result
in a specific combination of sorption properties, namely,
(1) a ratio of sorption of n-hexane to o-xylene, on a
volume percent basis, of greater than about 3, wherein
sorption is determined at a P/P$_0$ of 0.1 and at a
temperature of 50°C for n-hexane and 80°C for o-xylene and
(2) by the ability of selectively cracking 3-methylpentane
(3MP) in preference to the doubly branched 2,3-
dimethylbutane (DMB) at 1000°F and 1 atmosphere pressure
from a 1/1/1 weight ratio mixture of n-hexane/3-methyl-
pentane/2,3-dimethylbutane, with the ratio of rate
constants $k_{3MD}/k_{DMB}$ determined at a temperature of 538°C
(1000°F) being in excess of about 2.

The expression, "P/P$_0$", is accorded its usual
significance as described in the literature, for example,
in "The Dynamical Character of Adsorption" by J.H. deBoer,
2nd Edition, Oxford University Press (1968) and is the
relative pressure defined as the ratio of the partial
pressure of sorbate to the vapor pressure of sorbate at the
temperature of sorption.  The ratio of the rate constants,
$k_{3MP}/k_{DMB}$, is determined from 1st order kinetics, in the
usual manner, by the following equation:

$$k = (1/T_c) \ln (1/1-\epsilon)$$

where k is the rate constant for each component, $T_c$ is the
contact time and $\epsilon$ is the fractional conversion of each
component.

Zeolites conforming to these sorption requirements
include the naturally occurring zeolite ferrierite as well
as the synthetic zeolites ZSM-22, ZSM-23 and ZSM-35.  These

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zeolites are at least partly in the acid or hydrogen form when they are used in the present process.

The preparation and properties of zeolite ZSM-22 are described in U.S. Patent No. 4,810,357 (Chester) to which reference is made for such a description.

The synthetic zeolite ZSM-23 is described in U.S. Patent Nos. 4,076,842 and 4,104,151 to which reference is made for a description of this zeolite, its preparation and properties.

The intermediate pore-size synthetic crystalline material designated ZSM-35 ("zeolite ZSM-35" or simply "ZSM-35"), is described in U.S. patent No. 4,016,245, to which reference is made for a description of this zeolite and its preparation. The synthesis of SAPO-11 is described in U.S. Patent Nos. 4,943,424 and 4,440,871. The synthesis of SAPO-41 is described in U.S. Patent No. 4,440,871.

Ferrierite is a naturally-occurring mineral, described in the literature, see, e.g., D.W. Breck, ZEOLITE MOLECULAR SIEVES, John Wiley and Sons (1974), pages 125-127, 146, 219 and 625, to which reference is made for a description of this zeolite.

The dewaxing catalysts used in the shape-selective catalytic dewaxing preferably include a metal hydrogenation-dehydrogenation component. Although it may not be strictly necessary to promote the selective cracking reactions, the presence of this component has been found to be desirable to promote certain isomerization reactions which contribute to the synergy of the two catalyst dewaxing system. The presence of the metal component leads to product improvement, especially VI, and stability as well as helping to retard catalyst aging. The shape-selective, catalytic dewaxing is normally carried out in the presence of hydrogen under pressure. The metal will be preferably platinum or palladium. The amount of the metal component will typically be 0.1 to 10 percent by weight. Matrix materials and binders may be employed as necessary.

Shape selective dewaxing using the highly constrained,

highly shape-selective catalysts may be carried out in the
same general manner as other catalytic dewaxing processes,
such as those described above for the initial isomerization
phase.    Reference is made to U.S. Patent 4,919,788 for a
more extended discussion of the shape-selective catalytic
dewaxing step.

The degree of conversion to lower boiling species in
the dewaxing stage will vary according to the extent of
dewaxing desired at this point, i.e. on the difference
between the target pour point and the pour point of the
effluent from the isomerization stage.  It will also depend
upon the selectivity of the shape-selective catalyst which
is used.  At lower product pour points, and with relatively
less selective dewaxing catalysts, higher conversions and
correspondingly higher hydrogen consumptions will be
encountered.

After the pour point of the oil has been reduced to the
desired value by selective dewaxing, the dewaxed oil may be
subjected to treatments such as hydrotreating, in order to
remove color bodies and produce a lube product of the
desired characteristics.  Fractionation may be employed to
remove light ends and to meet volatility specifications.

Products

The products from the process are high VI, low pour
point materials which are obtained in excellent yield.
Besides having excellent viscometric properties they are
also highly stable, both oxidatively and thermally and to
ultraviolet light.  VI values in the range of 130 to 150
are typically obtained with the preferred wax feeds to the
process and values of at least 140, are readily achievable
with product yields of at least 50 wt%, usually at least 60
wt%, based on the original wax feed.

EXAMPLES

Example 1

A low-acidity zeolite beta-containing catalyst was prepared by first extruding a mixture of 65 parts by weight of zeolite beta with 35 parts by weight silica ($SiO_2$). The zeolite beta used in this preparation has a $SiO_2:Al_2O_3$ ratio of 600, an average crystal size of 1-3 microns as measured using scanning electron microscopy (SEM). Details of the synthesis are given in U.S. patents 5,232,579, 5,164,169, and 5,164,170. The mixture of zeolite beta and silica was mixed with an aqueous caustic solution to form a paste and extruded following standard procedures known to those skilled in the art of catalyst preparation. The extrudate was dried for 8 hours at 250°F, contacted with 5 v/v of a 1N $NH_4NO_3$ solution to reduce its sodium level. The sodium-reduced extrudate was then heated in $N_2$ to 482°C (900°F) and held there for 3 hours before exposure to air at 538°C (1000°F) for 6 hours to decompose the organic compounds used in the preparation of the zeolite beta. This catalyst was then exposed to 100% steam at 101 kPa₄ (0 psig) for a sufficient time (24 hours) to reduce its alpha activity to below 15.

This steam-deactivated zeolite beta containing material was then exchanged with an aqueous solution of platinum tetrammine chloride dihydrate maintained at a pH of between 7-8. The platinum exchanged catalyst was rinsed with water to remove chlorides and then heated to 349°C (660°F) in air and held there for 3 hours. The final catalyst contained 0.6 wt% platinum and has properties given in Table 4.

Table 4

Silica-Bound Pt/β Catalyst Properties

| Catalyst | Example 1 | Example 2 |
|---|---|---|
| Platinum, wt% | 0.5 | 0.5 |
| Sodium, ppm | 130 | 245 |
| Surface Area, $m^2/g$ | 318 | 316 |
| Pore Volume, cc/g | – | 0.97 |
| Alpha (prior to Pt Addition) | 13 | 8 |
| Crystal Size, $\mu$ | 1-3 | 0.05 |

Example 2

A zeolite beta-containing catalyst was prepared by
first extruding a mixture of 65 parts by weight of zeolite
beta with 35 parts by weight silica ($SiO_2$). The zeolite
beta used in this preparation had a $SiO_2:Al_2O_3$ ratio of 50,
an average crystal size of less than 0.05 microns as
measured using SEM, and was synthesized following standard
procedures for MIDW-grade zeolite beta. The mixture of
zeolite beta and silica was mixed with an aqueous caustic
solution to form a paste and extruded following standard
procedures known to those in the catalyst art. The
extrudate was dried for 8 hours at 121°C (250°F). The
sodium-containing extrudates were then heated in $N_2$ to
482°C (900°F) and held there for 3 hours before exposure to
air at 538°C (1000°F) for 6 hours to decompose the organic
compounds used in the preparation of the zeolite beta.
This catalyst was then exposed to an 2M aqueous solution of
oxalic acid for a total of 6 hours at 71°C (160°F). The
oxalic-acid treated zeolite beta catalyst was then heated
to 538°C (1000°F) for 2 hours. This material had an alpha
value less then 10 and a sodium content of 525 ppmw.

This oxalic acid-treated zeolite beta catalyst was then
exchanged with an aqueous solution of platinum tetrammine
chloride dihydrate maintained at a pH of between 5-6. The
platinum exchanged catalyst was rinsed with water to remove

chlorides and then heated to 349°C (660°F) in air and held
there for 3 hours. The final catalyst contained 0.5 wt%
platinum and has properties given in Table 4, supra.

Example 3

A slack wax derived from solvent dewaxing a 97cSt (450
SUS) heavy neutral furfural raffinate was hydrocracked at
mild severity to reduce its sulfur and nitrogen contents.
Conditions for the mild hydrocracking step were: 2 LHSV,
404°C (760°F), 13891 kPa$_a$ (2000 psig H$_2$) partial pressure.
Properties of the slack wax and the stripped hydrocracked
product are given by Table 5.

The mild hydrocracking step converted 16% of the slack
wax feed to products boiling below 343°C (650°F) and also
converted 17% of the wax in the feed. Wax conversion and
lube yield are calculated by the following equations.
Dewaxed oil yield was corrected to a 0°F pour point for
consistency.

$$\text{Wax Conversion} = 100x \ \frac{\text{Wax Content of Feed - Wax Content of Reaction Product}}{\text{Wax Content of Feed}}$$

Wax Yield = (Yield of Distillation Bottoms on Waxy Feed)

   x (Yield of Oil Free Wax From Solvent Dewaxing on Solvent Dewaxer Feed Basis)

Lube Yield = 100 - Wax Yield - 650°F+ Conversion Measured By Simulated Distillation

## Table 5

### Feed Stock Properties

| | 450 Heavy Neutral Slack Wax | Mildly Hydrocracker 450 Heavy Neutral Slack Wax |
|---|---|---|
| **Description** | | |
| Oil Content on 343°C+ (650°F+) Basis, % | 38 | 48 |
| Nitrogen, ppm | 68 | <7 |
| Sulfur, ppm | 1920 | <20 |
| **Simulated Distillation, °C** | | |
| IBP | 366 | 128 |
| 5% Off | 420 | 245 |
| 10% | 441 | 312 |
| 20% | 459 | 397 |
| 50% | 495 | 463 |
| 90% | 550 | 527 |
| FBP | 586 | 572 |
| **343°F+ Solvent Dewaxed Oil** | | |
| Kinematic Viscosity at 100°C, cSt | 11.3 | 6.1 |
| VI at -17.78°C (0°F) Pour | 92 | 138 |
| Yield, wt% Heavy Neutral Slack Wax | 37 | 33 |
| 343°C (650°F+) Conversion, % | – | 16 |
| Wax Conversion, % | – | 17 |

### Example 4

The mildly hydrocracked slack wax of Example 3 was reacted over the Pt/$\beta$ catalysts of Example 1 and 2 in separate experiments. Reaction conditions were 13891 kPa (2000 psig) and 1 LHSV for the catalyst of Example 1 and 1.25 LHSV for the catalyst of Example 2. Catalyst temperature was varied to effect changes in reaction severity. Prior to the introduction of liquid feed, both catalysts were presulfided with a mixture of 2 vol% $H_2S$/98 vol% $H_2$ to a maximum temperature of 371°C (700°F).

The reactor effluent from these experiments was
analyzed by simulated distillation to determine the
conversion to 343°C (650°F-) products and then distilled to
a nominal 343°C (650°F) cutpoint. Wax and lube yields and
wax conversions were calculated based on the equations of
Example 3 and are given by Table 6. The Figure illustrates
the relative dependence of lube yield on wax conversion for
the two catalysts.

The wax isomerization selectivity of the small crystal
catalyst (Example 2) was significantly higher than that of
the large crystal catalyst (Example 1). Lube yield peaked
at 64% for the small crystal Pt/$\beta$ catalyst while reaching
only 52% for the large crystal catalyst. Consistent with
the sequential reaction network of isomerization followed
by shape-selective cracking, both catalysts gave similar
yields at low wax conversions (less than 40%). However, as
the reaction severity was increased, the rate of cracking
in the large crystal catalyst relative to the isomerization
rate increased substantially so that at 50% wax conversion,
the rate of creation of lube by isomerization matched the
rate of lube loss by cracking. Increasing the wax
conversion beyond that point resulted in a decrease in lube
yield. In contrast, the ratio of isomerization to cracking
remained high for the small crystal catalyst up to high wax
conversions. The rates of the two reactions did not become
equivalent until 80% wax conversion was reached.

The practical application of the invention, beyond the
obvious higher yields for the small crystal catalyst, is
the catalyst's ability to selectively function at high wax
conversion. This reduces the amount of wax recycle and
reduces the size of the reactors required to produce a
given quantity of high VI base stock.

Zeolitic acidity can also play an important role in
determining isomerization selectivity. While the large
crystal Pt/$\beta$ catalyst had a higher alpha value compared to
the small crystal version (13 vs. 8), it is likely that the
selectivity difference observed between the catalysts was

not primarily a function of acidity. The difference in alpha values is not significantly large.

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## Table 6

### Wax Isomerization Selectivity of Silica-Bound Pt/β Catalysts

#### Example 1 Catalyst (1-3μ, 13∝)

5

| Pt/β Temp., °C | 343°C+ Conv. Over Pt/β % | Wax Conv. Over Pt/β % | 343°C+ Lube Yield % HNSW | 343°C+Lube VI at-17.78°C Pour |
|---|---|---|---|---|
| 313 | 1 | 26 | 46 | 141 |
| 316 | 3 | 34 | 49 | 142 |
| 322 | 5 | 45 | 52 | 144 |
| 325 | 10 | 51 | 51 | 142 |
| 333 | 21 | 63 | 48 | 143 |

10

#### Example 2 Catalyst (0.05 μ, 8∝)

15

| Pt/β Temp., °C | 343°C+ Conv. Over Pt/β % | Wax Conv. Over Pt/β % | 343°C+ Lube Yield % HNSW | 343°C+ Lube VI at -17.78°C (0°F) Pour |
|---|---|---|---|---|
| 307 | 3 | 30 | 46 | 144 |
| 312 | 4 | 49 | 54 | 145 |
| 321 | 11 | 75 | 61 | 142 |
| 324 | 12 | 84 | 64 | 144 |
| 324 | 15 | 82 | 61 | 142 |
| 327 | 18 | 86 | 61 | 142 |
| 329 | 24 | 93 | 59 | 141 |

20

WHAT IS CLAIMED IS:

1.   A process for producing a high Viscosity Index (VI)
lubricant from a waxy hydrocarbon feed having a wax content
of at least 20%, which comprises catalytically dewaxing
waxy paraffins present in the feed primarily by
isomerization, in the presence of hydrogen and in the
presence of a low acidity large pore molecular sieve having
a crystal size of less than 0.1 micron, an alpha value of
not more than 30 and containing a noble metal hydrogenation
component.

2.   The process of claim 1 wherein the large pore
molecular sieve possesses at least one pore channel of 12-
membered oxygen rings.

3.   The process of claim 1, wherein the large pore
molecular sieve is zeolite beta.

4.   The process of claim 3, wherein the zeolite beta has an
alpha value of not greater than 20.

5.   The process claim 1, wherein the large pore molecular
sieve has a crystal size less than 0.05 micron.

6.   The process of claim 1, wherein the large pore
molecular sieve is a low acidity zeolite beta which has
been steamed, having a framework silica:alumina ratio of at
least 200:1.

7.   The process of claim 1, in which the large pore
molecular sieve comprises a boron-containing zeolite beta
isomerization catalyst in which the boron is present as a
framework component of the zeolite beta.

8.   The process of claim 1, in which the large pore
molecular sieve comprises from 0.3 to 2 wt% Pt on a support
comprising zeolite beta.

9.   The process of claim 1 in which the feed comprises a
waxy hydrocarbon feed having a wax content of at least 40
wt% and an aromatic content of less than 25 wt%.

10.   The process of claim 1 wherein the feedstock is
selected from the group consisting of a slack wax, deoiled
wax, wax from Fischer-Tropsch process, foots oils,
petrolatum, vacuum gas oil, or a raffinate from solvent
extraction of a vacuum distillate.

11.   The process of claim 1, in which the process is
carried out in the presence of hydrogen to convert from 40
to 90 wt% of the wax contained in the feed.

12.   The process of claim 1, wherein conditions include a
hydrogen partial pressure ranging from 4238 to 20786 kPa.
(600 to 3000 psig) and a temperature from 288°C to 427°C
(550 to 800 °F).

13.   The process of claim 1 in which the catalytically
dewaxed feed is subjected to further selective dewaxing to
achieve target pour point.

14.   The process of claim 13, in which dewaxing is
accomplished by either solvent or catalytic means.

15.   The process of claim 1, in which the catalytically
dewaxed feed is hydrotreated by contacting it with a
catalyst comprising a metal hydrogenation component on a
porous support material at a pressure in the range from
about 3549 to about 20786 kPa, (500 to about 3000 psig), a
reaction temperature in the range from about 260°C to about
427°C (500°F to about 800°F), a space velocity which is in

a range from about 0.1 to about 10 LHSV, and a once-through
hydrogen circulation rate which extends from about 178 to
about 1780 n.1.1.$^{-1}$ (1000 SCF/B to about 10,000SCF/B), in
order to improve the thermal and oxidative stability of the
5    lubricant.

16.   The process of claim 13, in which the feed is
hydrotreated following selective dewaxing by contacting it
with a catalyst comprising a metal hydrogenation component
on a porous support material at a pressure in the range
10    from about 3549 to about 20786 kPa. (500 to about 3000
psig), a reaction temperature in the range from about 260°C
to about 427°C (500°F to about 800°F), a space velocity
which is in a range from about 0.1 to about 10 LHSV, and a
once-through hydrogen circulation rate which extends from
15    about 178 to about 1780 n.1.1.$^{-1}$ (1000 SCF/B) to about
10,000SCF/B, in order to improve the thermal and oxidative
stability of the lubricant.

17.   A process for producing a high Viscosity Index (VI)
lubricant from a waxy hydrocarbon feed having a wax content
20    of at least 20 wt%, the process comprising the following
steps:
        (a) hydrocracking of the feed in order to reduce its
nitrogen content as well as to remove naphthenic and
aromatic components, thereby improving VI, the
25    hydrocracking process comprising contacting the feed with a
catalyst composed of a metal hydrogenation component on an
acidic support;
        (b)  catalytically dewaxing waxy paraffins present in
the feed primarily by isomerization, in the presence of
30    hydrogen and in the presence of a low acidity large pore
molecular sieve having a crystal size of less than 0.1
micron, an alpha value of not more than 30 and containing a
noble metal hydrogen component.

18.   The process of claim 17, wherein the large pore
molecular sieve possesses at least one pore channel of 12-
membered oxygen rings.

19.   The process of claim 17, wherein the large pore
molecular sieve is zeolite beta.

20.   The process of claim 19, wherein the zeolite beta has
an alpha value of not greater than 20.

21.   The process of claim 17, wherein the large pore
molecular sieve is a low acidity zeolite beta which has
been steamed, having a framework silica:alumina ratio of at
least 200:1.

22.   The process of claim 17, in which the large pore
molecular sieve comprises from 0.3 to 2 wt% Pt on a support
comprising zeolite beta.

23.   The process of claim 17, wherein the feedstock is
selected from the group consisting of a slack wax, deoiled
wax, foots oil, wax from Fischer-Tropsch process,
petrolatum, vacuum gas oil, or a raffinate from solvent
extraction of a vacuum distillate.

24.    The process of claim 17, wherein conditions of step
(b) include a hydrogen partial pressure ranging from 4238
to 20786 kPa$_a$ (600 to 3000 psig) and a temperature from
288°C to 427°C (550 to 800°F).

25.   The process of claim 17 in which the effluent of step
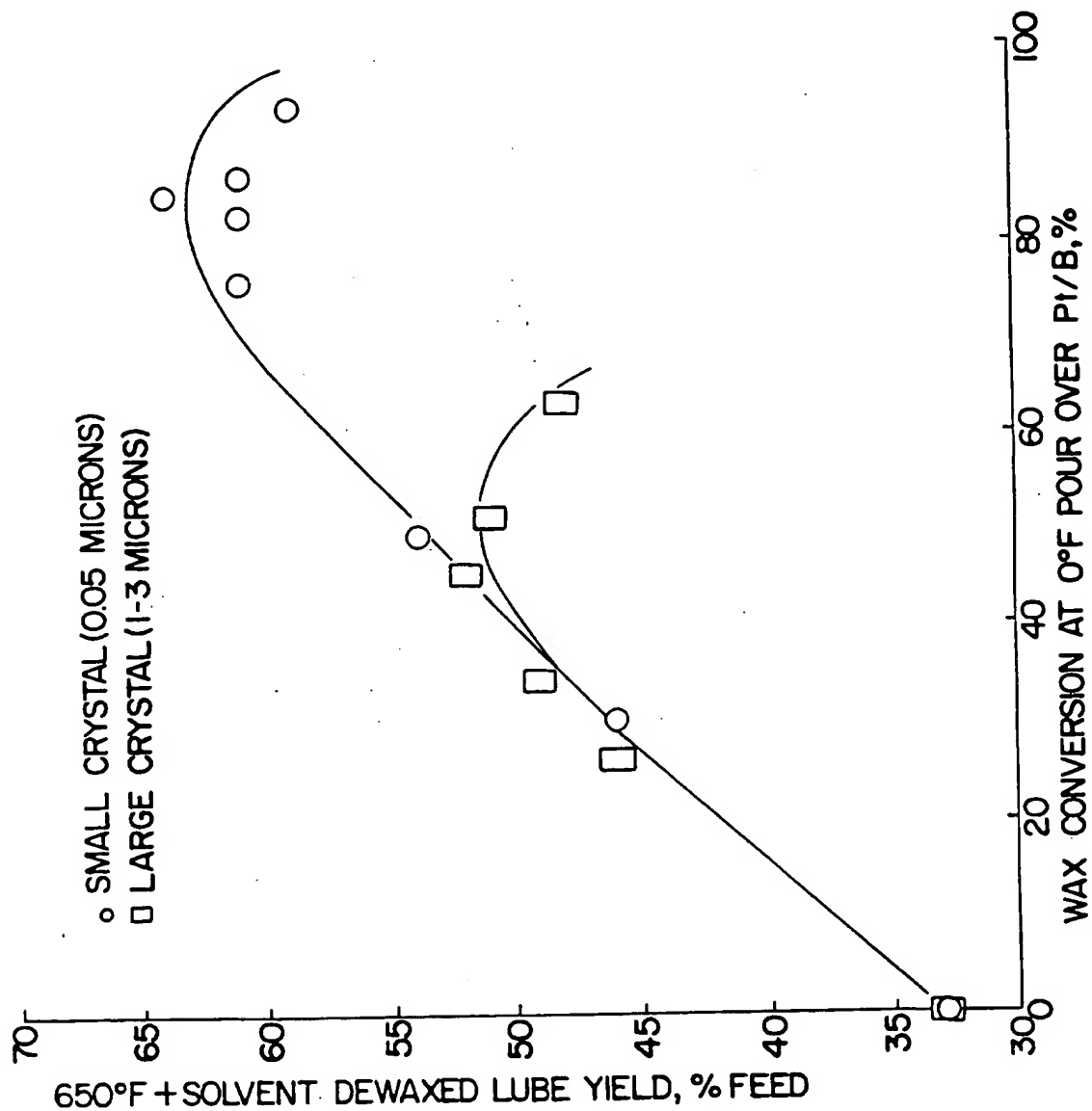(b) is subjected to further selective dewaxing to achieve
target pour point.

26.   The process of claim 25, in which dewaxing is
accomplished by either solvent or catalytic means.

27.  The process of claim 17, in which at least a portion
of the effluent of step (b) is hydrotreated by contacting
it with a catalyst comprising a metal hydrogenation
component on a porous support material at a pressure in the
5    range from about 3549 to about 20786 kPa, (500 to about
3000 psig), a reaction temperature in the range from about
260°C to 427°C (500°F to about 800°F), a space velocity
which is in a range from about 0.1 to about 10 LHSV, and a
once-through hydrogen circulation rate which extends from
10   about 178 to 1780 n.l.l.$^{-1}$ (1000 SCF/B to about 10,000
SCF/B), in order to improve the thermal and oxidative
stability of the lubricant.

28.  The process of claim 25 in which the effluent of step
(b) of claim 17 is subjected, following further selective
15   dewaxing to hydrotreating by contacting it with a catalyst
comprising a metal hydrogenation component on a porous
support material at a pressure in the range from about 3549
to about 20786 kPa, (500 to about 3000 psig), a reaction
temperature in the range from about 260°C to 427°C (500°F
20   to about 800°F), a space velocity which is in a range from
about 0.1 to about 10 LHSV, and a once-through hydrogen
circulation rate which extends from about 178 to 1780
n.l.l.$^{-1}$ (1000 SCF/B to about 10,000SCF/B), in order to
improve the thermal and oxidative stability of the
25   lubricant.

o SMALL CRYSTAL (0.05 MICRONS)
□ LARGE CRYSTAL (1-3 MICRONS)

WAX CONVERSION AT 0°F POUR OVER Pt/B, %

650°F + SOLVENT DEWAXED LUBE YIELD, % FEED

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/12823

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10G 73/00, 73/38

US CL :208/28, 58, 60, 138

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/28, 58, 60, 138

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US, A, 5,275,719 (BAKER, JR. ET AL.) 04 January 1994, col. 4, lines 61-68; col. 5, lines 1-55; col. 6, lines 10-45; col. 8, lines 63-68; col. 9, line 1 through col. 10, line 68; col. 14, lines 23-53; col. 15, lines 3-7 and 49-68; col. 16, lines 1-21 and 49-65; col. 17, lines 4-47; and col. 18, lines 20-37 and 51-63. | 1-27 |
| Y | US, A, 5,282,958 (SANTILLI ET AL.) 01 February 1994, col. 4, lines 20-44 and col. 5, lines 61-65. | 1-27 |
| A | US, A, 4,851,109 (CHEN ET AL.) 25 July 1989. | 1-27 |
| A | US, A, 4,983,274 (CHEN ET AL.) 08 January 1991. | 1-27 |

[X] Further documents are listed in the continuation of Box C.    [ ] See patent family annex.

| | |
|---|---|
| * Special categories of cited documents: | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| "A" document defining the general state of the art which is not considered to be of particular relevance | |
| "E" earlier document published on or after the international filing date | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "O" document referring to an oral disclosure, use, exhibition or other means | |
| "P" document published prior to the international filing date but later than the priority date claimed | "&" document member of the same patent family |

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 16 NOVEMBER 1995 | 24 JAN 1996 |

| Name and mailing address of the ISA/US | Authorized officer |
|---|---|
| Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 | WALTER GRIFFIN |
| Facsimile No. (703) 305-3230 | Telephone No. (703) 308-0661 |

Form PCT/ISA/210 (second sheet)(July 1992)*

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|---|---|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US, A, 5,302,279 (DEGNAN ET AL.) 12 April 1994. | 1-27 |
| P,A | US, A, 5,362,378 (BORGHARD ET AL.) 08 November 1994. | 1-27 |

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/12823

**Box I  Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 28
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II  Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**   ☐ The additional search fees were accompanied by the applicant's protest.
                        ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)*

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS: search terms: dewaxing, low acidity zeolite beta, crystal size, zeolite beta

STN-APIPAT: search terms: zeolite beta, hydrodewaxing, acidity/basicity